Year-End Report | *For the Period March 1, 1964 to December 1, 1964*

EMBRITTLEMENT BY LIQUID METALS

Prepared for:

UNITED STATES NAVY
OFFICE OF NAVAL RESEARCH
METALLURGY BRANCH
WASHINGTON, D.C.

CONTRACT Nonr-4408(00)
PROJECT Nr-036-058

STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA

SRI

Best
Available
Copy

STANFORD RESEARCH INSTITUTE

MENLO PARK, CALIFORNIA

SRI

December 31, 1964

Year-End Report | *For the Period March 1, 1964 to December 1, 1964*

EMBRITTLEMENT BY LIQUID METALS

Prepared for:

UNITED STATES NAVY
OFFICE OF NAVAL RESEARCH
METALLURGY BRANCH
WASHINGTON, D.C.

CONTRACT Nonr-4408(00)
PROJECT Nr-036-058

By: W. R. GOGGIN

SRI Project PMU-4925

Approved: A. E. GORUM, DIRECTOR
MATERIAL SCIENCES DIVISION

Copy No. 56

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

ABSTRACT

An electron microscopic investigation of the mechanics of liquid metal embrittlement is described. Specimen preparations, techniques, and tentative conclusions are reported on the aluminum-gallium couple.

INTRODUCTION

Liquid-metal embrittlement is the premature failure of a metallic body when subjected to a liquid-metal environment. Attempts to understand the mechanisms of an embrittling reaction have been mainly limited to macroscopic observations and mechanical tests. Some fundamental studies of the embrittlement process have been conducted, but as yet a complete atomic mechanism of embrittlement by a liquid metal remains uncertain. No single couple of a particular liquid and solid metal has been studied in sufficient detail to provide a clear relationship between the nature of embrittlement and certain important variables (temperature, prior history, chemistry of solid and liquid metal).

This research program, being conducted under the auspices of the Office of Naval Research, is a study of a particular couple (aluminum-gallium) utilizing techniques of transmission electron microscopy.

BACKGROUND

Most metals and alloys are susceptible to liquid metal embrittlement; however, certain conditions (e.g., proper selection of the liquid metal, temperature, stress) vary from alloy to alloy.

Many mechanical tests and macroscopic observations have been made on embrittled metals for the purpose of gaining some insight on the mechanisms of the embrittling process. The fracture process has been described as a brittle fracture, generally caused by intercrystalline cracking. Stress-strain tests on unwetted metals and metals wetted with liquid metals have shown that ductility, at fracture, is severely decreased by a liquid metal environment. It was found that ductility sharply decreased as the available supply of liquid metal increased. Yield strength and work-hardening rates remained unaffected; however, the fracture stress can be lower than the yield stress if sufficient liquid (metal) exists. When the supply of liquid metal was bountiful, the test specimens often fractured at stresses below the normal yield stress.

Macroscopic observations have shown several variables to be strong rate-controlling parameters. Some of these are:

1. Wetting behavior of the liquid metal
2. Temperature
3. Grain size
4. Stress

The first condition indicates that effective wetting is necessary to establish an intimate interface between the liquid and solid metals. An impenetrable surface layer, or complete immiscibility in the solid and liquid states would prohibit wetting, and thus constitute defenses against liquid-metal embrittlement.

Since embrittlement has been seen to exhibit strong dependence on temperature, it was shown by experiment that transport of the liquid metal appears to be the major rate-controlling parameter. Under conditions of constant stress, time-to-fracture was found to decrease as the temperature was raised.

The grain size dependence of liquid metal embrittlement was investigated (for a brass-mercury couple) and the fracture stress was observed to decrease as the grain diameter increased over a limited range.

The importance of stress as a major rate-controlling parameter was shown by time-to-fracture date: The time-to-fracture decreased sharply with increases of an externally applied stress.

A cursory literature survey of this field yields a wealth of information; however, a basic understanding of the kinetics of embrittlement by liquid metals has not been established. No single embrittlement couple has been studied in detail to provide a clear relationship among the several major variables.

The objective of this research program is to investigate the influence of liquid metals on the brittle fracture behavior of solid metals and alloys, and to attempt to gain a fundamental understanding of the embrittlement process.

WORK PERFORMED

Materials

The aluminum-gallium couple was chosen for this study in order to satisfy several stringent instrumental requirements of electron microscopy. The solid metal (aluminum) was chosen as a compromise among the following requirements:

1. Medium atomic weight (for electron transmission requirements)

2. Ease and reproducibility of forming thin films (0.000005-inch-thick needed for electron microscopy) from bulk specimens

3. High electrical conductivity (for elimination of electrostatic charge in electron transmission studies)

4. Practicality as an industrial or structural metal

The liquid metal (gallium) was chosen because of the following requirements:

1. Good wetting behavior with aluminum in the solid state (necessary for liquid metal embrittlement)

2. Low vapor pressure in a vacuum system (necessary in order to keep contamination rate to a minimum and to prevent evaporation in an electron microscope at a pressure level of 10^{-5} Torr)

3. Liquid metal must have melting point slightly above room temperature (in order to liquefy metal under the heat of electron bombardment in an electron microscope); the melting point of gallium is 29.8°C

4. The liquid metal must have a higher atomic scattering factor, or higher mass absorption coefficient, than the solid metal for diffraction studies in order to develop sufficient image contrast on film records

Aluminum of high purity (99.998% from Kaiser Aluminum Company, Oakland, California) and gallium (99.999% from Electronic Space Products, Inc., Los Angeles, California) were used in this study.

Techniques

Specimen preparations for electron microscopy were accomplished as follows. The aluminum was rolled to 0.010 inch in thickness, annealed and/or recrystallized (for grain growth), and electropolished in one part perchloric acid, four parts ethyl alcohol at -10°C, using standard techniques. Suitable sections of thickness, 0.000005 inch or less, were cut and mounted on a tensile device for insertion into the electron microscope. Liquid gallium was applied by one of two possible methods:

1. Vapor deposition in a vacuum evaporator
2. Deposition by a miniature heated probe.

It was found that transport could be followed more closely by the second deposition technique. Vacuum evaporation deposited a uniformly thick layer of gallium with the result that small amounts of the liquid transfer could not be followed closely because of low image contrast. Deposition by the miniature heated probe deposited a single particle of molton gallium at a selected locale, and diffusion paths were plainly seen to lead from this deposit.

An Hitachi HU-11 electron microscope operating at a voltage of 100 kV was used in this study. Test specimens were strained in tension during observation in the electron microscope on a tensile device capable of + 10% strain. The mild temperature increase necessary to melt the gallium (m.p. 29.8°C) was accomplished by controlling the current density of the electron beam, and occurred at a minimum beam current of 30 μA.

Air oxidation of the thin aluminum foils was kept to a minimum by storing the test specimens in ethyl alcohol. Mounting of the test specimens and application of liquid gallium was done in the minimum time possible (one minute) and the tensile assembly was immediately placed in a vacuum chamber of the electron microscope. This treatment yielded good test specimens with a shallow surface oxide which did not inhibit the formation of the intimate interface necessary for liquid metal embrittlement.

Experimental Observations

Several cursory macroscopic tests were conducted to visualize the speed of fracture and to observe its dependence on the type of stress (compressive or tensile).

Figure 1 is a photograph of a 1/4" x 1/2" x 5" bar of 7075-T6 aluminum alloy, cold rolled 3%, and bent as shown. With liquid gallium applied to each face, fracture occurred only on the surface exposed to residual tensile stresses. This behavior is well substantiated by more exacting work in the literature. Fracture occurred instantaneously and was accomplished by an audible tick.

A similar test conducted at a temperature below the melting point of gallium produced no fracture until the temperature was raised above 30^{o}C, the melting temperature of gallium.

Some simple bend tests on annealed bars of 2024-T6 and 1100 aluminum alloys produced similar results when gallium was deposited on the convex surfaces under tensile stresses. It was noted that fracture was exclusively intergranular, and the fracture terminated near the neutral axis (i.e., approximately midway between the surfaces under tensile and compressive stresses).

Several of the fracture surfaces were removed and examined with X-ray techniques, with the intent of identifying any intermetallic phase produced by the solid metal-liquid metal reaction. No such intermetallic was noted.

A typical electron microscopic observation began with a fully annealed (stress free) specimen placed in the tensile assembly. The gentle heating necessary to melt the gallium was accomplished by increasing the electronic current density until the gallium was seen to wet the aluminum surface. Generally, the gallium was placed at the edge of the foil, as in Fig. 2. The test specimen was then strained gradually until fracture occurred.

The fracture always initiated at the gallium deposit, and traversed the specimen at an orientation of approximately 90° to the tensile axis. The crack propagation velocity was too high for normal sequential photographic studies; however, some typical "after-the-event" photomicrographs are presented in Figs. 3, 4, 5, and 6.

Some interesting observations have been made from these photographs. Figures 3, 4, 5, and 6 exhibit a "clean" fracture surface characteristic of liquid metal embrittlement. The fracture surface appears to be free of the "serrated" edge typical of the shear fracture of an unwetted aluminum specimen, as in Fig. 7. In addition, Figs. 3 and 4 show the fracture to be intercrystalline in nature.

Observations indicate that the crack propagation continues until the supply of gallium is exhausted. This is evidenced in Figs. 8 and 9. Figure 8 is the blunt end of a crack in a thicker part of the specimen. This type of fracture is characterized by blunt-ended cracks, which appear to be free of liquid gallium. If a thin layer of gallium remains at the crack tip, its presence is beyond the limits of detection of conventional electron microscopy and electron diffraction. Figure 9 is an electron micrograph of the fracture surface taken a few microns distant from the crack tip of Fig. 8. Along its surface are seen the torn remnants of the surface oxide of aluminum, with droplets of liquid gallium held in suspension. After cooling to solidify the gallium, attempts to detect intermetallic formation by electron diffraction studies yielded no evidence of alloying.

Further studies of the catastrophic embrittling behavior will be conducted with high speed photographic techniques to determine if fracture is of a continuous or discontinuous nature. In a discontinuous failure, the embrittling liquid would initiate a crack which could propagate without the presence of a liquid, and the crack would be stopped by the plastic relaxation of the matrix near the crack tip. Upon transport of the embrittling liquid to the crack tip, the crack would again be initiated.

Accompanying the primary fracture of the specimen foil, a second phenomenon has been observed. This involves a slower mechanism controlled by the transport of liquid gallium along surfaces and grain boundaries. This latter behavior is a corrosion process leading to the eventual dissolution of grain boundaries and subsequent dismemberment of the polycrystal.

Figures 10 and 11 represent two photomicrographs taken over a 10-minute interval. The specimen had been stressed and the primary fracture had occurred at another place on the specimen. The elastic stresses remaining in this area were sufficient to drive the corrosion process. The open areas represent voids or thin areas along inclined grain boundaries, and indicate that the individual crystal grains, or groups of grains, are shearing (grain boundary shearing) out of the plane of the thin foil.

Figure 12 depicts the role grain boundaries play as diffusion short-circuits. In this case, liquid gallium traveled along the grain boundaries and diffused out over the nearby surface. The beginning of grain boundary dissolution is evidenced by the development of open areas.

Figures 13 through 16 characterize advanced stages of grain boundary dissolution. Figures 13 and 14 show a crystalline grain, which after having moved vertically away from the plane of the specimen, is held to the plane by forces of adhesion with the liquid gallium, and merely glides away from its original location. A closer examination of Fig. 13 demonstrates that the aluminum crystal has been divorced from its oxide layer, which remains bonded to the whole oxide layer, and as the crystal glides away it trails a meniscus of liquid gallium. These micrographs reveal the fact that liquid gallium wets both the aluminum and the aluminum oxide, and the chemistry of the aluminum-gallium couple is sufficiently reactive to separate aluminum from its normally tenacious, parasitic oxide.

Figures 15 and 16 reveal individual crystalline grains suspended in a sea of liquid gallium. The original aluminum oxide layer remains unbroken and provides the sole support for this colloidal suspension of aluminum microcrystals.

CONCLUSIONS

The conclusions given at this time are only hypotheses requiring substantiation through additional experiments.

Electron microscopic investigations of the liquid metal embrittlement behavior of aluminum-gallium couples have revealed brittle fracture processes occurring through intercrystalline attack by the rapid transport of liquid gallium. After the primary brittle fracture, a secondary, slower rate, corrosion cracking process occurred that bears a striking similarity to several of the characteristics of the primary embrittlement.

Both processes appear to be actuated by the mass transport of liquid gallium along grain boundaries. In the cases of the primary liquid metal embrittlement, the crack velocity is so rapid that normal diffusion rates, even along grain boundaries, are surpassed in order to supply gallium to the propagating crack. Evidence to support this lies in the fact that no excess gallium is momentarily available at a particular site along the fracture surface to diffuse over the surface of the specimen as in Figs. 3 and 4. On the other hand, the slower moving corrosion behavior along grain boundaries yields some of its excess gallium to the surface, as in Fig. 12.

This similarity of behavior indicates enhancement of liquid metal transport along grain boundaries by many orders of magnitude for the embrittlement process. It is felt that the crystallographic misorientation across a grain boundary does not supply a mechanism for the diffusion enhancement necessary for embrittlement, since the same misorientation occurs in the corrosion behavior. A vacancy emission mechanism from grain boundaries under normal stresses (i.e., grain boundaries lying 90° to the tension axis) could supply vacant lattice sites to the approaching gallium atoms at high rates, in order to sustain an atom-vacancy exchange mechanism of diffusion.

Another possible mode of rapid crack propagation would involve the formation of an aluminum-gallium intermetallic phase at a grain boundary. As the bonds of the second phase were established, the forces of cohesion between aluminum grains would decrease and would result in the eventual separation of grains to create a crack-void. To date, there is no evidence of an intermetallic formation; however, a monolayer of an intermetallic phase would be undetectable by conventional techniques.

The rapid mass transport of liquid gallium may be "driven" by a surface tension mechanism, involving an effort to maintain the equilibrium dihedral angle at the gallium meniscus. A propagating crack would carry its necessary supply of gallium in the form of a droplet wetted to the aluminum and bound by forces of surface tension. The crack velocity would then decrease to zero as the supply of liquid metal was expended. This mechanism could account for the apparently high estimate of enhancement of liquid metal transport observed in liquid metal embrittlement. If this were the case, the actual mechanism of embrittlement could be separated from its accompanying, but independent, slower-rate transport phenomena.

It is therefore evident that more studies along this approach should be conducted.

FUTURE WORK

Subsequent research will be directed toward an understanding of the mass transport enhancement phenomena observed in liquid metal embrittlement. To achieve these ends, efforts are being directed toward high speed photography with the hope of photographically recording a propagating crack.

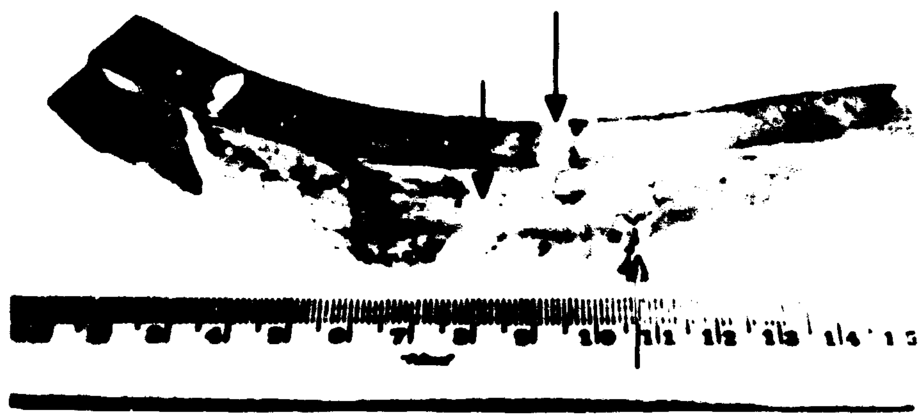
Efforts are under way for the preparation of single crystal and bicrystalline specimens of aluminum. Attempts to initiate transgranular fracture in coarse-grained aluminum have only succeeded in promoting the corrosion process, but not the high speed fracture; additional tests are necessary. The dependence of fracture path on grain boundary orientation (with respect to the tensile axis) of bicrystals is being investigated The fracture behavior of single crystals in a liquid metal environment will also be studied. The recent observations of Westwood[1] indicate that this could be a very fruitful approach.

Experimental work has commenced on an embrittling couple with a body-centered-cubic crystal structure (β-brass-mercury) to determine differences in fractural behavior in completely ductile materials (e.g., aluminum) and materials which may exhibit brittle fracture (e.g., β-brass).

Future investigations will include grain size dependence of fracture stress for an embrittlement couple. Extension of these data and/or experiments will be made to several aluminum alloys and brasses as time allows.

---

1. Westwood, et al., Complex-Ion Embrittlement of Silver Chloride November 1964. RIAS MARTIN CO. under ONR Contract Nonr-4162(00).



TA-4928-1

FIG. 1 1/4" × 1/2" × 5" 7075-T6 ALUMINUM ALLOY COLD ROLLED 3%, BENT TO EXPOSE SURFACE WITH RESIDUAL TENSILE STRESSES. Arrows indicate liquid gallium.

7568

FIG. 2 LIQUID GALLIUM AT EDGE OF THIN FILM OF ALUMINUM. Mag. 4,000 X

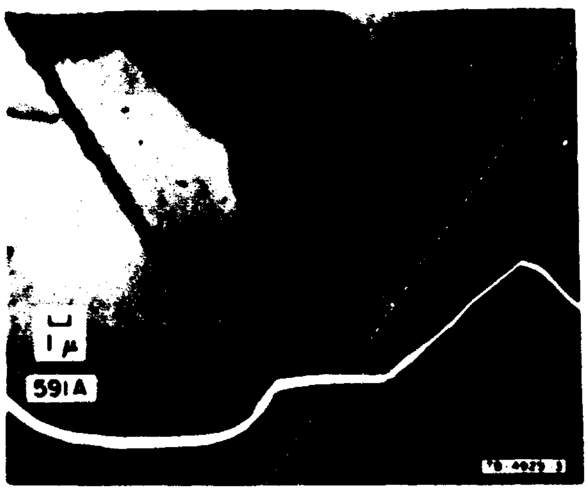


FIG. 3

FIG. 4

FIG. 5

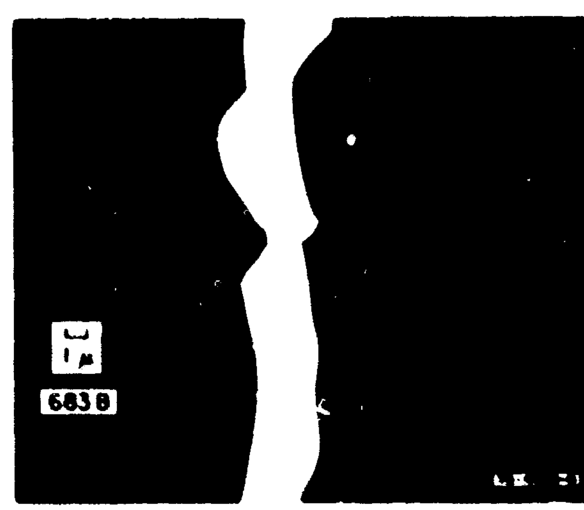


FIG. 6

LIQUID METAL EMBRITTLEMENT FRACTURE SHOWING INTERCRYSTALLINE CRACK PATH. Note little or no liquid gallium on surface area adjacent to crack.

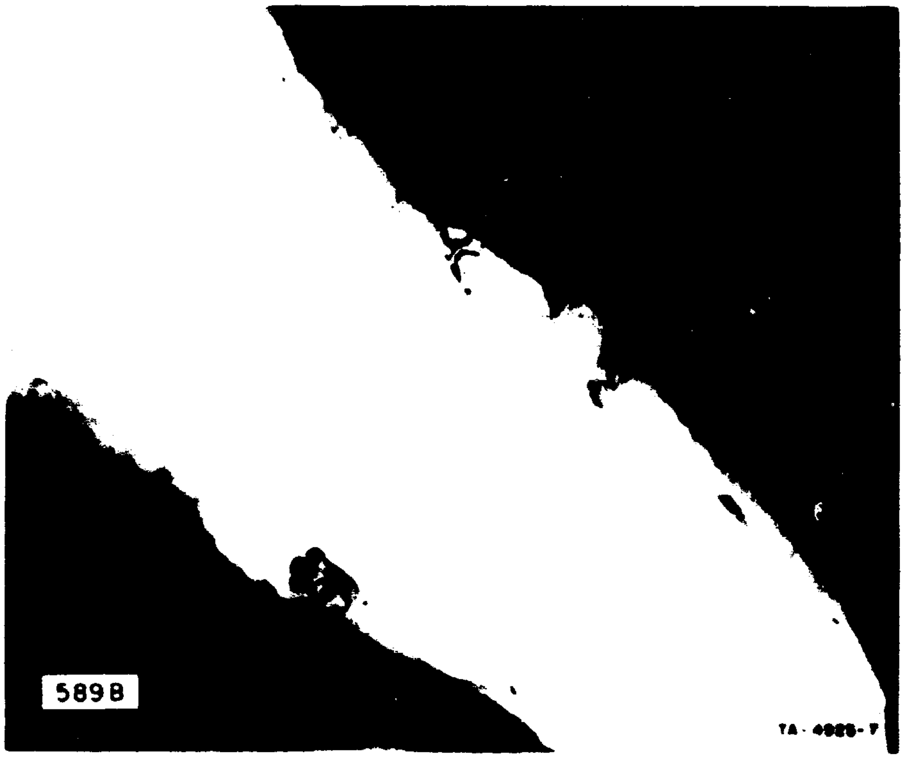


FIG. 7 SHEAR TYPE OF FRACTURE EXHIBITING "SERRATED" EDGE. Photo of unwetted aluminum specimen pulled in tension under identical conditions. Mag. 5,000 X

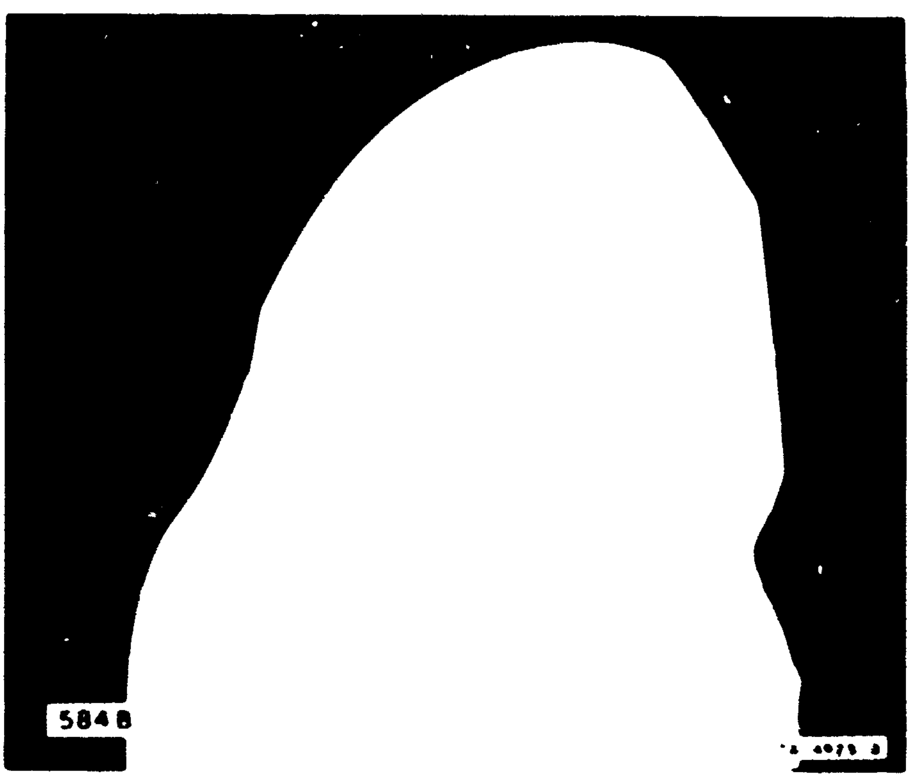


FIG. 8 CRACK TIP WITH NO EVIDENCE OF GALLIUM PRESENT. Mag. 5,000 X

FIG. 9 MICROGRAPH TAKEN SEVERAL MICRONS FROM CRACK TIP
Edge shows residue of torn aluminum oxide film with large amount of liquid gallium present. Mag. 5,000 X

FIG. 10 BEGINNING OF CORROSION PROCESS. Mag. 10,000 X

FIG. 11 PHOTO TAKEN 10 MINUTES AFTER FIG. 10. Mag. 10,000 X

FIG. 12 GRAIN BOUNDARY DIFFUSION. Dark contrast signifies diffusing gallium. Mag. 4,000 X

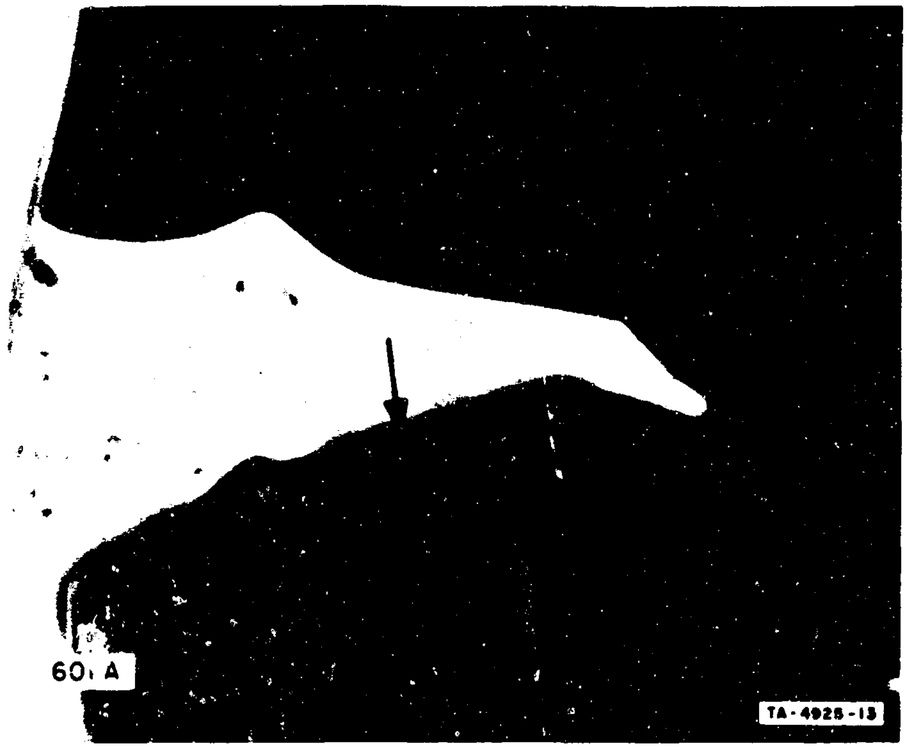


FIG. 13

FIG. 14

DISSOLUTION OF POLYCRYSTAL BY GALLIUM DIFFUSION.
Arrows indicate meniscus of gallium. Mag. 18,000 X

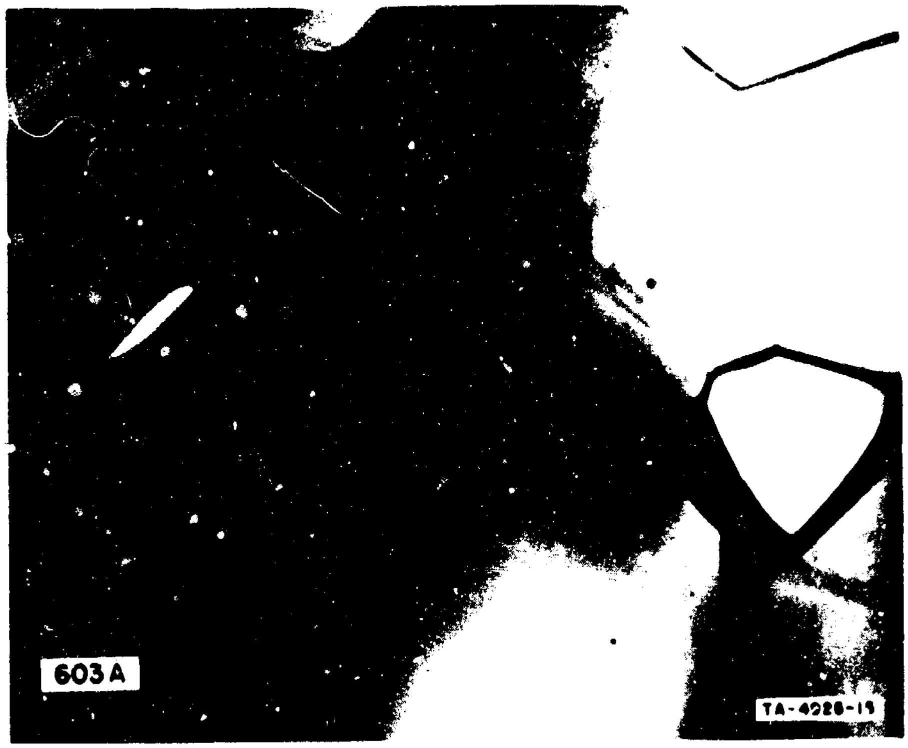


FIG. 15

FIG. 16

MICROGRAPHS OF COMPLETELY DISSOCIATED POLYCRYSTALLINE SPECIMEN. Mag. 27,000 X

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author) Stanford Research Institute	2a. REPORT SECURITY CLASSIFICATION Unclassified
	2b GROUP

3 REPORT TITLE

Embrittlement by Liquid Metals

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)

Summary Report. March 1, 1964 - December 1, 1964

5 AUTHOR(S) (Last name, first name, initial)

Goggin, William R.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
December 31, 1964	19	1

8a. CONTRACT OR GRANT NO. Nonr-4408(00)	9a. ORIGINATOR'S REPORT NUMBER(S) SRI Project PMU 4925
b. PROJECT NO. Nr-036-058	
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	

10. AVAILABILITY/LIMITATION NOTICES

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Office of Naval Research

13 ABSTRACT

An electron microscopic investigation of the mechanics of liquid metal embrittlement is described. Specimen preparations, techniques, and tentative conclusions are reported on the aluminum-gallium couple.

DD FORM 1 JAN 64 1473

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Embrittlement by Liquid Metals						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2a. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.

7a. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8a. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through ________________."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through ________________."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through ________________."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (*TS*), (*S*), (*C*), or (*U*).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.

STANFORD RESEARCH INSTITUTE

MENLO PARK CALIFORNIA

Regional Offices and Laboratories

Southern California Laboratories
820 Mission Street
South Pasadena, California 91031

Washington Office
808-17th Street, N.W.
Washington, D.C. 20006

New York Office
270 Park Avenue, Room 1770
New York, New York 10017

Detroit Office
1025 East Maple Road
Birmingham, Michigan 48011

European Office
Pelikanstrasse 37
Zurich 1, Switzerland

Japan Office
Nomura Security Building, 6th Floor
1-1 Nihonbashidori, Chuo ku
Tokyo, Japan

Retained Representatives

Toronto, Ontario, Canada
Cyril A. Ing
67 Yonge Street, Room 710
Toronto 1, Ontario, Canada

Milan, Italy
Lorenzo Franceschini
Via Macedonio Melloni, 49
Milan, Italy